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Direct Laser Patterning on Opaque Substrate in Two-Photon Polymerization

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Introduction

Recently, increasing trends toward direct nano-patterning processes which refer to the fabrication of nano-patterns without photomasks or stencils have been reported,[1-8] and they lead to mass-productive and cost-effective processes related to various research fields such as nanotechnology, biotechnology, information technology, and micro/nanofluidic devices and systems. Photolithography using photomasks has been considered as the most successful method in microfabrication since its invention. Although the process has many advantages and usefulness, it requires inevitably complex procedures and high cost photomask for precise patterning. Also it is difficult to achieve the minimum resolution of patterns under submicron due to the diffraction limit of a beam.

So far, many works on the direct fabrication of nano-patterns have been conducted for breakthrough in nano/microfabrication: X-ray writing,[1] electron-beam lithography (EBL),[2,3] and extreme UV lithography (EUV)[4] are leading candidates. These techniques have the capability to generate extremely small feature less than 100 nm to several nm in size, but their developments into economical methods for cheap production of nanostructures still require substantial efforts. Nano-imprinting lithography (NIL) and soft-mold lithography (SML)[5-9] are considered as promising alternative lithography methods for fabricating nano-patterns cheaply and mass-productively, however the fabrication cost of high precision quartz stamps for imprinting and masters for replicating soft molds is very high. Also, these methods generally require secondary processes for eliminating residual layers after patterning processes.

In the past few years, some works[10-18] have been carried out in nanoscale fabrication technology using two-photon polymerization (TPP) induced by a femtosecond (fs) laser. It is well known that TPP has many advantages as a technique for direct fabrication of complex three-dimensional (3D) structures on a scale of several microns, which might be difficult to obtain using the conventional technologies.[10-13] Femtosecond laser pulses can be closely focused into the volume of liquid-state monomers so that the pulses initiate the chemical process for polymerization with the resolution of approximately 100 nm,[14] which is less than diffraction limit of a laser beam. By employing TPP, various 3D micro-structures have been reported; optical memories,[15] photonic crystals,[16] micro-rotors,[17] micro-oscillators,[18] and so on. However, in the majority of the works, the fabrication of 3-D micro-objects have been done onto transparent glass or quartz plate due to the use of immersion oil between an objective lens and a droplet of photocurable resin for achieving a high resolution. To the best of our knowledge, there are no available reports concerning the direct nano-patterning on the opaque surface using the TPP, which is generally more valuable for practical applications. In this work, the TPP with a top-down reverse (TDR) building technique is proposed for the direct fabrication of nano-precision patterns without any photomask on opaque substrates such as a silicon wafer. In the proposed process, patterns are designed using two-tone (black-and-white) bitmap formatted pictures, then they are transformed to voxel matrices which are consists of two kinds of components; '0' for laser off and '1' for laser on. Therefore, complex patterned shapes can be easily designed and fabricated by a voxel matrix scanning (VMS) method.[19] Furthermore, there are no residual layers after a developing process, which is an important advantage in direct laser writing processes. Also, the thickness of a pattern can be readily controlled, and various thickness distributions of patterns can be obtained by tuning process parameters; laser power, exposure time, and truncation amount under a substrate. Through the fabrication of several patterns by the TPP process with the TDR building technique, we have demonstrated the possibility of a high effective patterning technique for micro-electromechanical systems (MEMS) and various nano/micro applications with the resolution of approximately 110 nm.

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Experimental

Materials. The material for TPP used in this work was a mixture of a commercial urethane acrylate resin (SCR 500, Japan Synthetic Rubber Co.) and the photosensitizer TP-Flu-TP2 (0.1 wt%), which was synthesized from 2,7-dibromo-9,9-diethylhexyl-9H-fluorene and diphenyl(4-vinylphenyl) amine by the Heck reaction.[20]

TP-Flu-TP2. This photosensitizer has the ability to react at low laser power and with short exposure times, which makes it possible to obtain high resolution with the TPP procedure. The two-photon absorption (TPA) cross section, σ, of the TP-Flu-TP2 was found to be 954 GM (1 GM=1 $\times$ 10^{-50} cm^4 $\cdot$ sec/photon) at the wavelength of 940 nm, with UV absorption and fluorescence wavelengths of 411 and 472 nm, respectively.[12]

Laser Setup. An optical laser system for TPP is set up as illustrated in Figure 1. A mode-locked Ti:sapphire laser, which has an 800 nm wavelength, 80 MHz repetition, and less than 100 fs pulse width, is used as a beam source, and the beam is projected onto a galvano-mirror scanner to deflect its planar direction according to the controlled paths. The beam is then focused vertically with a high numerical aperture (NA) objective lens (NA 1.4, magnification 100) using a piezoelectric (PZT) stage. The exposure time of a beam is controlled by a galvano-shutter with stable exposure time of more than 1 ms. The shutter, scanner, and PZT stage were controlled by a computer system. An optical broadband isolator was used to block the backward flow of laser beam from surface reflection of each optical components, which prevents Ti: Sapphire from damaging. The situations of fabrication process and the position of focused beam are monitored exactly using the high magnifying CCD camera. The details for TDR building technique will be given in the section of results and discussion.

Results and Discussion

Two-photon absorption (TPA) is a popular multiple photon excitation phenomenon as a route for the initiation of photochemical changes. TPA induced by the fs-laser is commonly classified as simultaneous two-photon excitation; there is no real intermediate state, but a virtual intermediate state is created by the interaction of the absorbing species with the first photon. Only if the second photon arrives within the virtual state lifetime, about 10^{-15} s, can it be absorbed.[21] Therefore, it is apparent that the large photon flux density is required for the simultaneous two-photon excitation, which is the reason of employing the fs-laser in the TPP process. Ti:Sapphire lasers are widely used for inducing TPA because they carry an extremely large transient peak power, compared with continuous-wave and nanosecond pulses lasers, with a very short pulse width of approximately 100 fs or less. When a high intensity beam is closely focused into the volume of a liquid-state resin that is transparent to near infrared light, the photosensitizer chromophore that is generally used to enhance two-photon activation is excited by the simultaneous absorption of two photons, then emits fluorescent light around UV region for polymerization. The large photon flux density compensates the very small TPA cross-section in a focal region, which leads to a very high spatial resolution can be obtained, i.e. beneath the limit of diffraction of the light used in the TPP process.

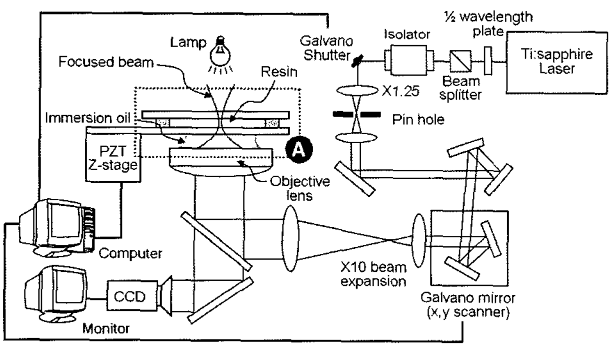

Figure 1. A schematic diagram of the optical laser system for the fabrication of nano-patterns.

As illustrated in Figure 2, a patterning part in the TPP system consists of two plates; a lower transparent plate (thin glass plate, less than 100 μm in thickness) and an upper opaque substrate (a transparent substrate is also possible). A focused beam is located on the surface of the upper sub-

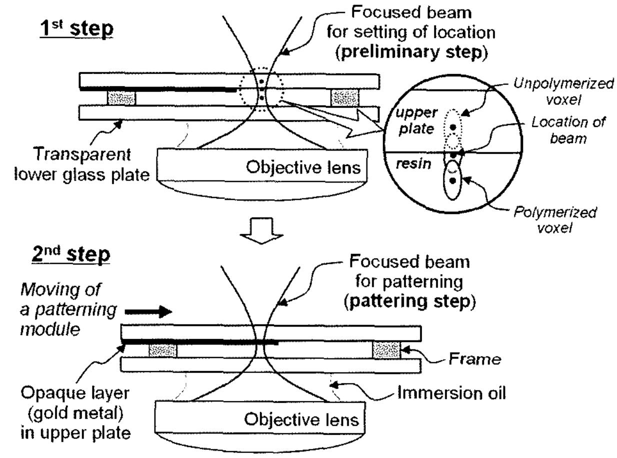

Figure 2. A schematic diagram of a detailed partial module of the laser system that is marked as 'A' in Figure 1. The patterning module consists of a lower glass plate (100 μm), a frame (100 μm), and an upper plate. A thin golden layer with 50 nm thickness is deposited as an opaque layer on the upper plate. Top down reverse (TDR) building procedure consists of two sequential steps for positioning of a focused beam and patterning on an opaque layer. The inset shows polymerized voxel shapes according the focal positions.

strate in order to pattern, employing the TDR building technique. The lower plate functions as separation of immersion oil and resins, so it essential for it to be transparent and thin, however it is not so for the upper plate. The TDR building procedure has two sequential steps; a preliminary step for positioning a focused beam on the upper plate and a patterning step on the upper plate. For the easy manipulation of beam location in the preliminary step, the upper plate was designed to have two parts as shown in Figure 2; an opaque part for patterning and a transparent part for monitoring of the location of a focused beam. In this work, the opaque part of the upper plate was fabricated by the deposition of gold on it with 50 nm thickness. Firstly, a closely focused laser beam is manipulated for the exact location on the transparent surface of the upper plate using the PZT-stage and the monitoring of CCD camera. The preliminary step for the location of a focused beam on an exact position is very important in the TDR building technique. As illustrated in the inserted circle of Figure 2, in case the focused beam spot is located inside of the upper plate, the polymerization does not occur. In another case, the beam spot is located far from the surface of upper plate more than voxel length, about 1 μm, the polymerization occurs in the volume of resins without adhesion to the upper plate, so the fabricated patterns are removed in the developing process. When the control of focal position is finished, for the next step, the upper plate is moved horizontally to locate the focused beam on the opaque part, in this work on the golden layer; then direct patterning is done on the upper substrate. After patterning by the TDR building technique, the remaining liquid-state monomer can be eliminated easily by dropping several ethanol droplets on the upper plate in a developing process.

TDR building technique utilizes the VMS method as a beam scanning method, which was proposed in our previous work.[19] In the VMS method, the raster graphics type of a voxel matrix transformed from a bitmap figure is scanned to fabricate patterns. The voxel matrix consists of two kinds of components, '0's for white pixels (no image part in a bitmap figure) and '1's for black pixels (image part for polymerization in a bitmap figure). The on/off control of laser beam is conducted employing the components of a voxel matrix; in case of '1', the shutter is open for polymerization, otherwise, the shutter is closed to stop the polymerization. Figure 3 explains the VMS procedure schematically.

To estimate the feasibility of the TDR building technique as a new direct patterning method applicable to semiconductor processes, several patterns have been fabricated directly on a gold layer. Figures 4(a) and 4(b) show the fluorescent optical images of obtained patterns on a golden layer. All patterns were fabricated with the conditions of laser power of 60 mW and exposure time of 1 ms; in which conditions the resolution of voxel is known to be about 150 nm in diameter. The fabricated map of England was measured using AFM to estimate its exact shape and surface roughness, as shown in Figure 4(c). AFM images show that the fabricated micro-England was 13.58 × 10.15 μm in vertical and horizontal directions, and its surface roughness was approximately 39 nm as an averaged-value of Ra, when a pitch between voxels was 24 nm. The surface quality of this level could generally satisfy the requirement of various patterning applications in MEMS. However, a good quality of the surface and interface is essential for micro-optical applications. A pitch between neighboring voxels affects the surface roughness of fabricated patterns in the TPP process, so this indicates that 39 nm is not considered as a limit of the surface roughness; however there is a method for improving the smoothness of patterns by overlapping voxels much closer than the given value.

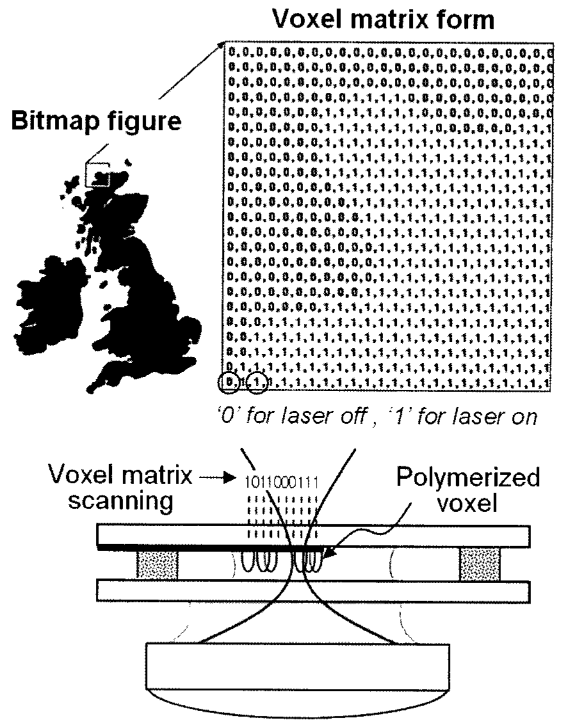

Figure 3. The bitmap file of a map of England is transformed into a voxel matrix form. The rectangular box is a part of the full voxel matrix that consists of two kinds of component; '1' for laser beam on and '0' for laser beam off. The underside diagram shows voxel matrix scanning (VMS) procedures; a laser beam is scanning along the row of a voxel matrix and a '1' represents the laser beam being on; a '0' the laser beam being off. The center of a voxel is located in the coordinate of each '1' of the voxel matrix.

The process parameters of the TPP process are known as exposure time, laser power, and truncation amount under substrates in the previous works.[19] The voxel shape can be expressed as eqs. (1) and (2) considering process parameters;[22,23]

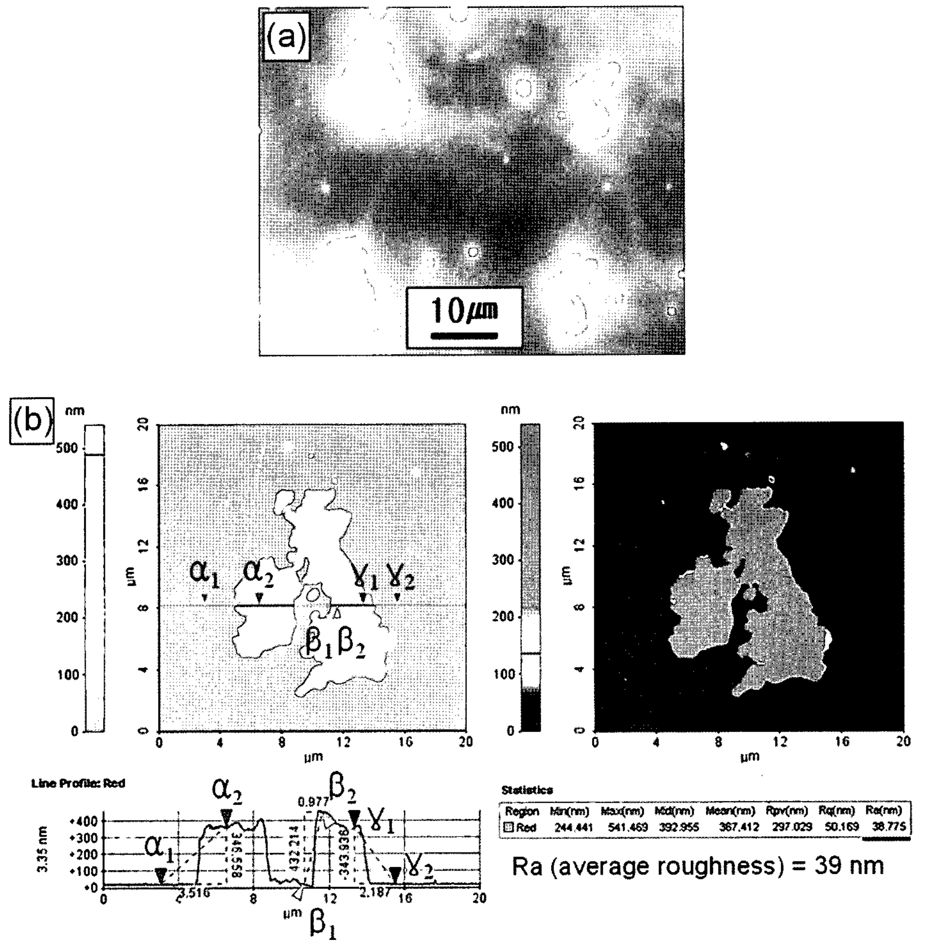

Figure 4. Images of various patterns on the thin gold layer, which are observed by an optical microscope; (a) an array of ring shapes amplified 2,000 times; (b) the map of England and the Korean peninsula amplified 1,000 times; (c) AFM images of the map of England. Its thickness is approximately 400 nm and its surface roughness is about 39 nm as Ra-value.

$$d(P,t,NA) = \frac{\lambda}{\pi\tan(\sin^{-1}(NA/n))}\left[\ln\left(\frac{4\pi^2P_t^2\cdot t\cdot[\tan(\sin^{-1}(NA/n))]^4}{E_{th}\cdot\lambda^4}\right)\right]^{\frac{1}{2}} \quad (1)$$

$$l(P,t,NA) = 2z = \frac{\lambda}{\pi[\tan(\sin^{-1}(NA/n))]^2}\left[\left(\frac{4\pi^2P_t^2\cdot t\cdot[\tan(\sin^{-1}(NA/n))]^4}{E_{th}\cdot\lambda^4}\right)^{\frac{1}{2}}-1\right]^{\frac{1}{2}} \quad (2)$$

where d, l, E_{th}, P_t, t, NA, n, and λ denote the voxel diameter, voxel length, threshold energy for polymerization, exposed laser power, exposure time, numerical aperture of objective lens, the index of refraction of the immersion oil, and wavelength, respectively. From the eqs. (1) and (2), the voxel diameter and length are steeply increased by the increase of laser power and exposure time in the field of threshold energy for polymerization.[22] And theoretical studies and experiments suggest that there are two different modes of growth determining the shape of voxels; focal spot duplication and voxel growth.[23,24] Therefore, various patterns, which have various line widths and heights, can be fabricated using the delicate control of process parameters.

Figure 5(a) shows that the variation of line width achieved under various conditions of laser power and exposure time. Until exposure time of 5 ms, the line width is rapidly changed as predicted in the theoretical studies, and with increasing of laser power and exposure time, the line width increased correspondingly in the range of 110 to 750 nm. The minimum width of line patterns was obtained as approximately 110 nm in the condition of laser power of 40 mW and exposure time of 1 ms. Some dots and lines, as depicted in Figure 5(b), were fabricated using the TPP process; the fabrication conditions of the first and the second quadrant in Figure 5(b) were laser power 60 mW and exposure time of 1 ms, and their aspect ratio was about 1.5; the third quadrant image shows line pat-

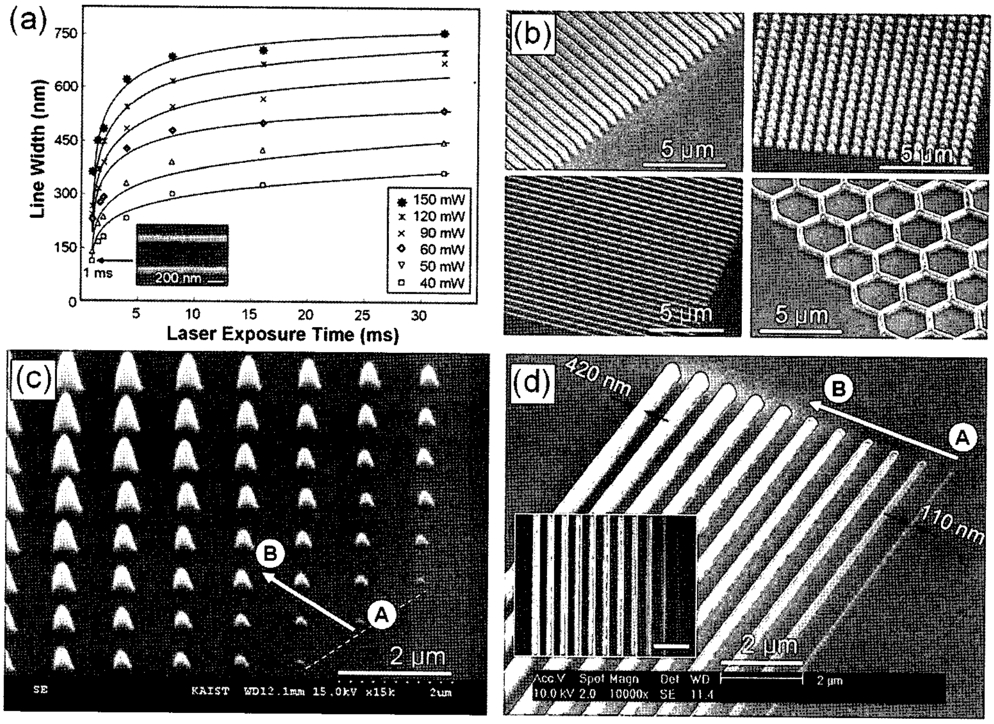

Figure 5. (a) Experimental results on the line width of patterns with various conditions of laser power and exposure time. Inset is a SEM image of fabricated line pattens under laser power of 40 mW and exposure time of 1 ms. (b) SEM images of various patterns: there is no residual layer. (c) and (d) show SEM images of dot and line patterns with inclined view, they are fabricated by ascending beam focal position step by step from 'A' to 'B'. An ascending amount of focal position in a step is 70 nm in dot patterns and 100 nm in line patterns. Inset in (d) is top view of line patterns and the scale bar is 2 μm.

terns fabricated in the conditions of laser power of 50 mW and exposure time of 1 ms, and their aspect ratio was about 1.0. Furthermore, the thickness of patterns can be controlled readily using a truncation amount of voxels which is determined by the position of a focused beam. Figures 5(c) and 5(d) show the SEM images of fabricated dot and line patterns elevating the laser focal position by steps in 70 and 100 nm, respectively. These results show that our technique enables to fabricate patterns that have multi-thickness distribution in a single process. Also, the line width of patterns can be reduced increasing the truncation amount, as shown in Figure 5(d), because the shape of voxel, which is an elementary component of patterns, is a revolution of ellipsoid.

Conclusions

In summary, we have presented a method for direct patterning on an opaque material without photomasks by a TDR building technique in the TPP process. The method is based on the two-photon polymerization process which is considered as a promising technology to fabricate 3D microstructures with the resolution of less than diffraction limits of a beam. The threshold energy region for polymerization is very narrow in the TPP. However, we observed that a refractive light on the opaque substrate is not a serious problem for the fine patterning in the TDR technique. Comparing to other direct patterning processes such as soft mold lithography and nano-imprinting lithography, there is no residual layer in the fabricated patterns by the proposed method. The resolution of patterns can be controlled by process parameters; laser power, exposure time, truncation amount, numerical aperture of objective lens for tightly focusing, and pitch between voxels. With increasing laser power, exposure time and numerical aperture of an objective lens, the line width and the thickness of patterns are increased, and the minimum line width achieved in this work was approximately 110 nm. The truncation amount of patterns has an effect on the thickness and precision of patterns. Some fabricated patterns by the TDR building technique in the TPP process show the possibility of applicable to direct patterning for various MEMS applications. Also, the surface roughness measured from a fabricated pattern was approximately 39 nm as an average value. It is feasible to improve the roughness by a reduction of pitch between voxels, and in the further studies, we will try to estimate the surface roughness of patterns related to the pitch of voxels for much more precise pattering.

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References

(1) R. F. Pease, *Jpn. J. Appl. Phys.*, **31**, 4103 (1992).
(2) M. D. Austin, H. Ge, W. Wu, M. Li, Z. Yu, D. Wasserman, S. A. Lyon, and S. Y. Chou, *Appl. Phys. Lett.*, **84**, 5299 (2004).
(3) B. K. Yoon, W. Hwang, Y. J. Park, J. Hwang, C. Park, and J. Chang, *Macromol. Res.*, **13**, 435 (2005).
(4) J. E. Bjorkholm, *Intel Techn. J. Q3*, **1988**, 1
(5) S. Y. Chou, P. R. Krauss, and P. J. Renstrom, *J. Vac. Sci. Techn. B*, **14**, 4129 (1996).
(6) A. Kumar and G. M. Whitesides, *Appl. Phys. Lett.*, **63**, 2002 (1993).
(7) Y. Xia, E. Kim, X. M. Zhao, J .A. Rogers, M. Prentiss, and G. M. Whitesides, *Science*, **273**, 347 (1996).
(8) X. M. Zhao, Y. Xia, and G. M. Whitesides, *Adv. Mater.*, **8**, 837 (1996).
(9) E. Kim, Y. Xia, and G. M. Whitesides, *Nature*, **376**, 581 (1995).
(10) S. Kawata, H. B. Sun, T. Tanaka, and K. Takadam, *Nature*, **412**, 697 (2001).
(11) J. Serbin, A. Egbert, A. Ostendorf, B. N. Chichkov, R. Houbertz, G. Domann, J. Schulz, C. Cronauer, L. Frohlich, and M. Popall, *Opt. Lett.*, **28**, 301 (2003).
(12) S. H. Park, T. W. Lim, D.-Y. Yang, H. J. Kong, and K.-S. Lee, *Polymer(Korea)*, **28**, 305 (2004).
(13) S. H. Park, T. W. Lim, S. H. Lee, D.-Y. Yang, S. W. Yi, H. J. Kong, and K.-S. Lee, *Polymer(Korea)*, **29**, 146 (2005).
(14) K. Takada, H. B. Sun, and S. Kawata, *Appl. Phys. Lett.*, **86**, 071122 (2005).
(15) A. S. Dvornikov and P. M. Rentzepis, *Opt. Commun.*, **119**, 341 (1995).
(16) H. B. Sun, S. Matsuo, and H. Misawa, *Appl. Phys. Lett.*, **74**, 786 (1999).
(17) P. Galajda and P. Ormos, *Appl. Phys. Lett.*, **78**, 249 (2001).
(18) H. B. Sun, K. Takada, and S. Kawata, *Appl. Phys. Lett.*, **79**, 3173 (2001).
(19) T. W. Lim, S. H. Park, and D.-Y. Yang, *Microelectron. Eng.*, **77**, 382 (2005).
(20) H. A. Dieck and R. F. Heck, *J. Am. Chem. Soc.*, **96**, 1133 (1974).
(21) V. K. Varadan, X. Jiang, and V. V. Varadan, *Microstreolithography and Other Fabrication Techniques for 3D MEMS,* John Wiley & Sons, Chichester, 2001.
(22) S. H. Park, S. H. Lee, D.-Y. Yang, H. J. Kong, and K.-S. Lee, *Appl. Phys. Lett.*, **87**, 154108 (2005).
(23) K.-S. Lee, R. H. Kim, D.-Y. Yang, and S. H. Park, *Polym. Adv. Technol.*, 2005, in press.
(24) H. B. Sun, K. Takada, M. S. Kim, K.-S. Lee, and S. Kawata, *Appl. Phys. Lett.*, **83**, 1104 (2003).